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L. Perera and Max L. Berkowitz

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ULTRA-FAST SOLVATION DYNAMICS IN A STOCKMAYER FLUID

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Abstract: Computer simulations of charge solvation dynamics in Stockmayer solvent display the existence of two time regimes. In this communication we show that the short time regime is due to inertial independent motion of solvent particles.

Dynamics of charge (or charge distribution) solvation is a subject of considerable interest [1]. Recent molecular dynamics computer simulation studies revealed that solvent relaxation occurs in two time regimes [2-7]. During the initial regime, which can be described by a Gaussian function, the relaxation occurs very fast (25-150 fs). The fast regime contributes about 60-80 % towards the total solvent relaxation and the motion of the solvent molecules in this regime has an inertial character. The short time regime is followed by a long time regime, which can be described by an exponential function. The motion of solvent molecules in this regime has a diffusional character. The two phase behavior of the solvent relaxation was observed in MD simulations performed in solvents such as water[2], acetonitrile[3], methanol[4] and methyl chloride [5]. Very recently the two regime behavior of solvent relaxation was also observed in MD simulations performed in simple polar fluids described by a Stockmayer potential [6-7]. The presence of two time regimes in the solvation dynamics was also confirmed by the experiment [8].

While the existance of the two regimes in the relaxation is firmly established, the nature of the solvent dynamics in these regimes is not completely clear. Thus for example, using the results of his simulations in acetonitrile, Maroncelli has assigned the fast regime to a small amplitude independent, inertial (mostly rotational) motion of molecules in the first solvation shell [3]. Contrary to this assignment Bagchi and Chandra recently proposed that the short time decay of the relaxation in simple Stockmayer solvents can be described in terms of collective excitation [9].

To separate between these two different proposed mechanisms we performed one extra set of non-equilibrium computer simulations in addition to our previous simulations [6] where we studied the dynamics of the Stockmayer solvent following a sudden change in the solute charge. In our previous study we performed three Non-Equilibrium Simulation sets NESI, NESII and NESIII in which we followed the time development of the normalized response function S(t) defined as

$$S(t) = \frac{\delta E(t) - \delta E(\infty)}{\delta E(0) - \delta E(\infty)} \tag{1}$$

In equation (1) $\delta E(t)$ is the fluctuation in the solvent-solute interaction energy at a given time t.

To study the effect of the rotational and translational degrees of freedom of the solvent we froze the translational motion in the first simulation (NESI). In NESII both rotational and translational motion participated in the relaxation. The Stockmayer solvent in our simulations was characterized (in reduced units) by a dipole moment $(\mu^*)^2 = 3.0$, a moment of inertia $I^* = 0.025$, a density $\rho^* = 0.822$ and a temperature $T^* = 1.15$. More details on the simulations were given in ref. [6]. In NESIII we changed the moment of inertia of the solvent in order to study the relative importance of the translational and rotational modes.

The additional simulation set performed now (NESIV) consisted of 50 trajectories which had the same starting configurations as the trajectories from the set NESI. The difference between the trajectories in NESIV set and NESI set is that the molecular dynamics in NESIV set was performed with no solvent-solvent interactions. Figure 1 displays the behavior of the relaxation function S(t) obtained from the sets NESI, NESII and NESIV. As we can see from this figure, up to ~0.09 ps (at this time the energy relaxed ~70%) the decay functions obtained from NESI and NESIV are practically indistinguishable. We also know from our previous work and from the other simulations that the main contribution into relaxation comes from the rotational motion of molecules in the first solvation shell (the difference in S(t) for the NESI and NESII is very small). Therefore from figure 1 we conclude that the initial relaxation in our system is due to the independent inertial rotational motion of solvent molecules.

To find out how large in amplitude is this rotational motion we present the average value of the rotational angle as a function of time in figure 2. As we can see from this figure, after 0.09 ps the average dislacement angle for the dipoles in the first solvation shell is ~45°, which is twice as large as the average displacement angle for the Stockmayer dipole in a sample of pure solvent under the same conditions. Also note that the average displacement angle for the dipoles in secondary shells around the ion is ~25°, the same value as in pure solvent. Due to the acceleration the average angular displacement of the first shell dipoles grows quickly and reaches its maximum value of ~120° overshooting the equilibrium value of ~85°. While the angular motion of the first shell dipoles is underdamped, the secondary shell dipoles display an overdamped motion.

The picture of the dynamic solvation of the ion in Stockmayer fluid that emerges from

our simulation is rather simple. Once the charge on the solute is turned on, the solvent dipoles of the first shell rush towards a favorable orientation along the field emanating from the ion. The motion of the solvent particles has an inertial independent character. The solvent particles practically do not see each other during the short time regime (~0.1 ps) and only after its completion the interaction between particles starts influencing their motion. At this time the motion becomes correlated. At long time scale the motion has diffusional character and this is reflected in a slow exponential decay of the relaxation function. Finally we want to mention that this picture of the solvent dynamics of the Stockmayer solvent is probably correct when a large perturbation ($\Delta q = 1.0$) is applied to the solute.

We thank Prof. B. Bagchi for providing us with the manuscript of ref. [9] prior to its publication. This work was supported by the Office of Naval Research.

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Figure captions.

Fig 1. Response function S(t) obtained from: NESII (solid line), NESI (dashed line) and NESIV (dotted line).

Fig 2. Average orientational angle of the dipole in the: first solvation shell (solid line), second solvation shell (dashed line) and third solvation shell (dotted line).
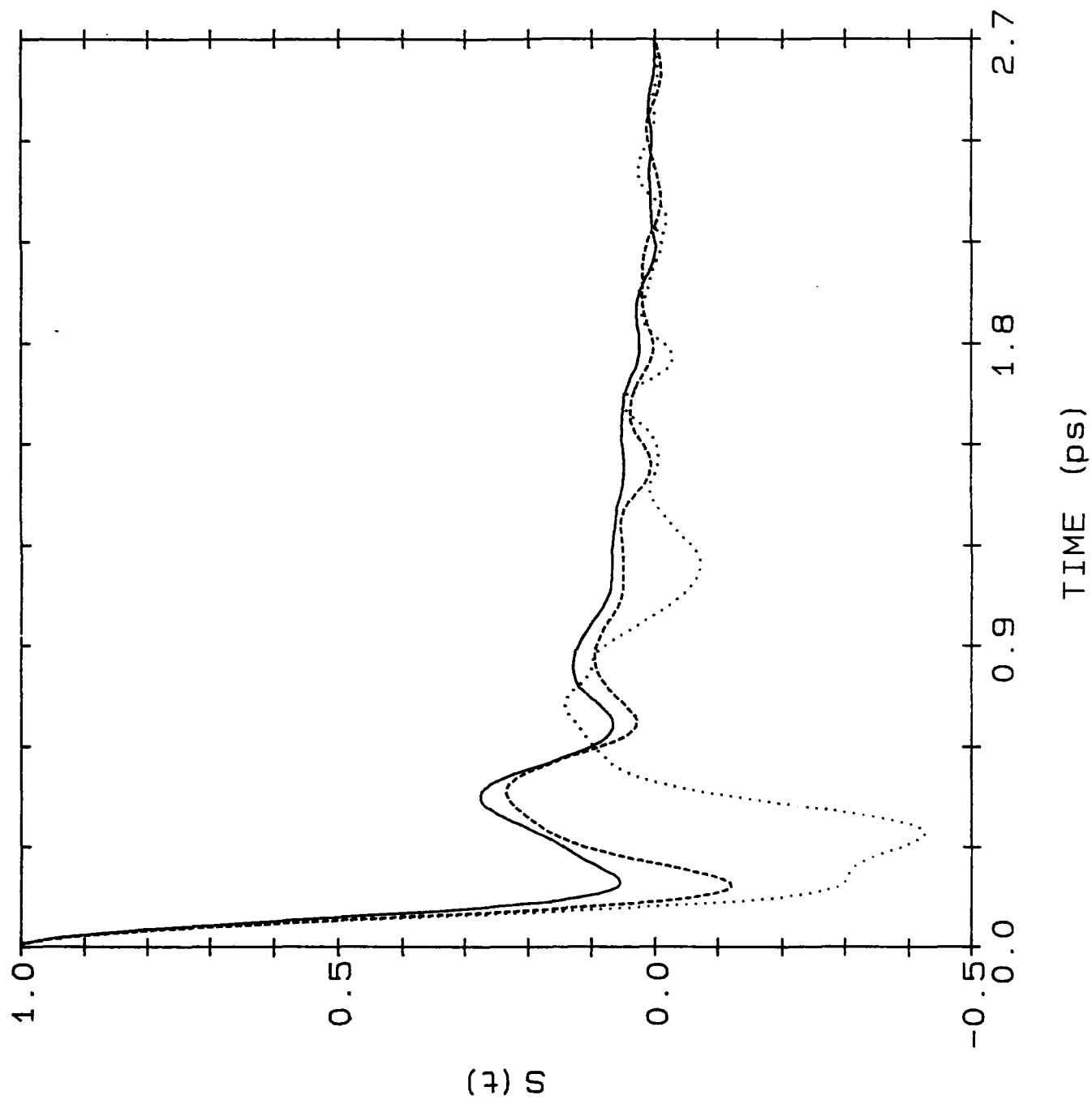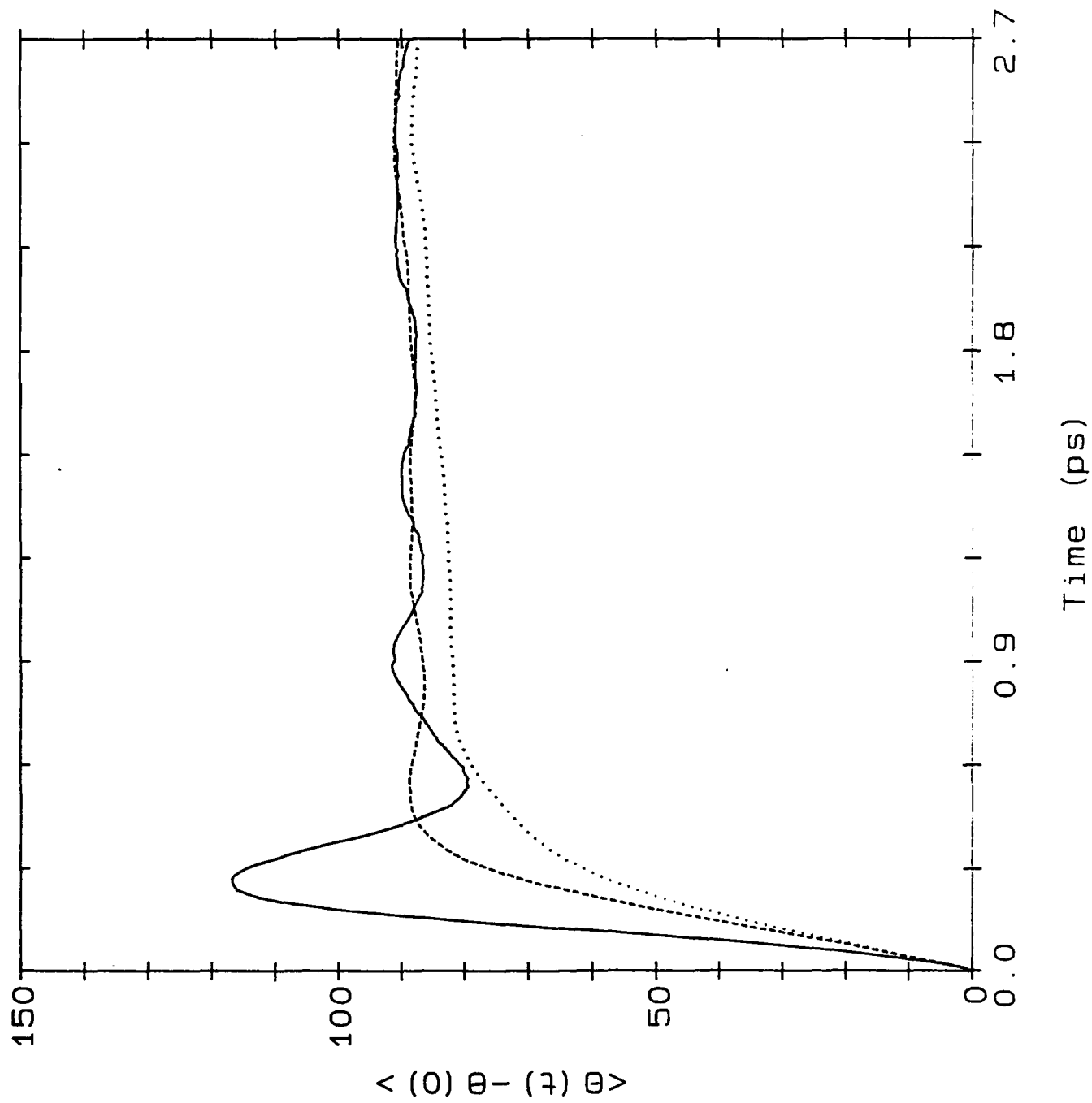
TIME (ps)

S (t)

Fig 1

Fig. 2

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